Potentials of anodic stripping voltammetry for the toxicological analysis of heavy metals

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SUMMARY

In the course of time different techniques have been proposed and used for the detection and quantitation of heavy metals in analytical toxicology. In chapter I these techniques have been described and it appeared that there is still a great need for a simple screening device as a convenient means to provide a heavy metal profile in forensic and clinical toxicology. Therefore the potentials of differential pulse anodic stripping voltammetry (DPASV) in these areas have been studied. This technique was chosen because it seemed to fulfill a number of important prerequisites for toxicological analysis, namely speed, simplicity, qualitative and quantitative information without the need for large financial investments. In addition, DPASV is capable of providing low detection limits.

The principles and theory of anodic stripping voltammetry and those of the differential pulse technique have been described in chapter II. In section II-3, polarography has been compared with anodic stripping voltammetry and it appeared that DPASV lends itself extremely well to the sensitive detection and quantitative determination of series of trace elements in toxicology both for acute and chronic poisoning cases as well as for studying normal levels of potentially toxic trace elements in biological samples. For those metals that cannot be determined by DPASV, differential pulse polarography represents a good, albeit somewhat less sensitive, alternative.

As standard addition is generally accepted for the quantitation of metals by DPASV, this method was also utilized in the present work. In chapter III, its principles have been discussed and the graphical method of standard addition has been compared with linear regression techniques based on a constant coefficient of variation of the measurements (weighted linear regression and a transformation model). For optimization of the standard addition method, assuming a common coefficient of variation, equations have been given to calculate - for a desired precision - the amount of standard to be added and the required number of replicate measurements.

Chapter IV describes a screening system for ten heavy metals, namely

antimony, bismuth, cadmium, copper, indium, lead mercury, thallium, tin and zinc, based on the measurements of peak potentials in two types of electrolyte solution and using two different electrodes (the hanging mercury drop electrode and the mercury film electrode). The first electrolyte solution is 0.6 *M* in hydrochloric acid, whereas the second one also contains ascorbic acid and ammonia to obtain a final pH-value of 4.5. For the detection of mercury, a mercury free electrode is required and the bare glassy carbon electrode has been used.

This screening system allows to distinguish rapidly from normal situations. A few heavy metals will be present in the majority of biological samples in a measurable quantity, such as copper, lead and zinc. If an extra peak is observed, or if peaks that are normally present are elevated, the intoxication can be identified in a short time.

The detection of tin is somewhat complicated as lead, which is nearly always present in biological fluids may interfere. Hence the amounts of interference has to be calculated first after which the contribution of lead to the combined lead-tin peak can be subtracted.

The quantitative possibilities for the determination of the above mentioned ten heavy metals with regard to the application to biological fluids have been described in chapter V. Starting from the screening system, for each metal the potentials of standard addition were studied by recording calibration plots. In order to obtain an impression of the accuracy and the precision of the quantitative determinations, some recovery experiments have been carried out usually at one concentration only. For thallium, however, recovery experiments have been carried out with three or four concentrations and not only in urine but also in plasma and whole blood.

It may be concluded that the quantitative determination of antimony, bismuth, indium, lead, thallium and tin can be carried out directly in urine without a destruction under the same experimental conditions as described for the qualitative screen in chapter IV. Irreproducible results were obtained for some of the other metals *directly* in urine. Yet, the observed interferences which can be attributed to the presence of organic compounds in the urine can be overcome by applying a destruction procedure.

For some quantitative assays it could be shown that DPASV could compete with AAS using a flame as well as with flameless AAS with regard to

precision and sensitivity.

In chapter VI some applications of DPASV to authentic clinical and forensic toxicological cases have been described.

In a case of Wilson's desease the influence of the therapeutic agent, D-penicillamine, on the copper analysis in urine has been studied. It appeared that D-penicillamine did not prevent the detection and quantitative determination of copper in urine, so that the efficacy of D-penicillamine on the copper excretion in urine can be followed by DPASV.

In a case of acute lead intoxication the antidote, calcium-edetate, prevented the direct quantitative determination of lead in urine. A destruction of the urine sample followed by the determination of lead by DPASV gave results that were in good agreement with AAS measurements.

In two cases of acute thallium poisoning, urinary thallium levels were measured by DPASV. The technique was found to lend itself very well for the detection and the quantitative determination of thallium over a wide concentration range. Faecal samples containing prussian blue, a widely used antidote for thallium intoxications, could be analysed by DPASV after a thorough destruction of the sample.